

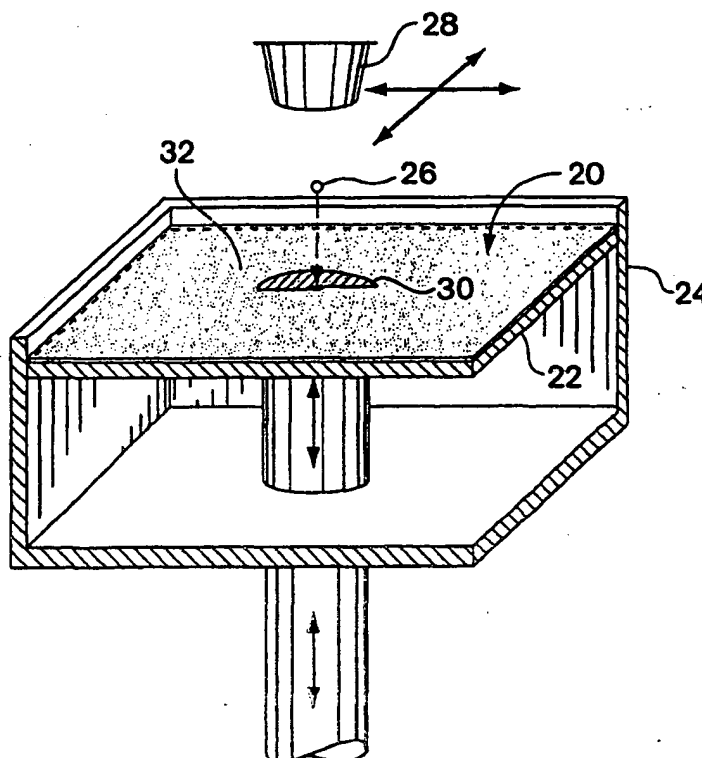


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(21) International Application Number: PCT/US99/20628 (22) International Filing Date: 9 September 1999 (09.09.99) (30) Priority Data: 09/182,295 29 October 1998 (29.10.98) US (71) Applicant: Z CORPORATION [US/US]; 35 Medford Street #213, Somerville, MA 02143 (US). (72) Inventors: BREDET, James, F.; 73 Templeton Parkway, Watertown, MA 02172 (US). ANDERSON, Timothy, C.; 155 Webster Avenue, Apt. 3, Cambridge, MA 02141 (US). RUSSELL, David, B.; 12 Winchester Street, Southboro, MA 01772 (US). (74) Agent: YOUNG, Michele, J.; Wolf, Greenfield & Sacks, P.C., 600 Atlantic Avenue, Boston, MA 02210 (US).		(81) Designated States: CA, JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>With amended claims.</i>

(54) Title: THREE DIMENSIONAL PRINTING MATERIAL SYSTEM AND METHOD**(57) Abstract**

The present invention is directed to a 3DPT™ three dimensional printing material system and method, and an article made therefrom. The method of the present invention includes building cross-sectional portions of a three-dimensional article, and assembling the individual cross-sectional areas in a layer-wise fashion to form a final article. The individual cross-sectional areas are built by using an ink-jet printhead to deliver an aqueous fluid to a particulate material that includes plaster.



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THREE DIMENSIONAL PRINTING MATERIAL SYSTEM AND METHOD

BACKGROUND

5 1.0 **Field Of The Invention**

This invention relates generally to rapid prototyping techniques, and more particularly to plaster-based Three Dimensional Printing materials and methods.

2.0 **Related Art**

10 The field of rapid prototyping involves the production of prototype articles and functional parts, as well as ceramic shell molds for metal casting, directly from computer-generated design data.

Two well-known methods for rapid prototyping include a selective laser sintering process and a liquid binder Three Dimensional Printing process (3DP™, trademark of Massachusetts Institute of Technology, Cambridge, Massachusetts). The techniques are
15 similar to the extent that they both use layering techniques to build three-dimensional articles. Both methods form successive thin cross sections of the desired article. The individual cross sections are formed by bonding together grains of a granular material on a flat surface of a bed of the granular material. Each layer is bonded to a previously formed layer to form the desired three-dimensional article at the same time as the grains of each layer are bonded
20 together. The laser-sintering and liquid binder techniques are advantageous because they create parts directly from computer-generated design data and can produce parts having complex geometries. Moreover, 3DP™ methods can be quicker and less expensive than conventional machining of prototype parts or production of cast or molded parts by conventional "hard" or "soft" tooling techniques which can take from a few weeks to several
25 months, depending on the complexity of the item.

3DP™ methods have been used to make ceramic molds for investment casting, thereby generating fully-functional metal parts. Additional uses have been contemplated for 3DP™ methods.

For example, 3DP™ methods may be useful in design-related fields where the articles
30 may be used for visualization, demonstration and mechanical prototyping. It may also be useful for making patterns for molding processes. 3DP™ methods may be further useful, for example, in the fields of medicine and dentistry, where expected outcomes may be modeled

inorganic. Typical organic binder materials are polymeric resins, or ceramic precursors such as polycarbosilazone. Inorganic binders are used where the binder is incorporated into the final articles; silica is typically used in such an application.

One advantage of using an ink-jet print head rather than a laser is that inexpensive
5 printheads are commercially available that have a plurality of spray nozzles used to deliver binder to the powder that are arranged side-by-side in a single print head. In selective laser sintering machines, only one laser, which delivers energy to the powder, is conventionally used. The combination of several spray nozzles increases the speed of liquid binder printing compared to laser-sintering by allowing a wider area to be printed at one time. In addition,
10 the liquid binder printing equipment is much less expensive than the laser equipment due to the high cost of the laser and the high cost of the related beam deflection optics and controls.

However, the liquid binder printing technique has a serious reliability problem associated with the spray nozzles becoming clogged with the binder and/or powder material. Clogging occurs when binders having high levels of suspended solids are used. The problem
15 with clogging requires frequent interruptions of the build in order to clean the spray nozzle. The clogging problem increases the time and labor required to build parts and to maintain the equipment. Therefore, although the liquid binder printing technique represents an advance in speed and cost over the selective laser sintering process, it suffers from reliability problems that slow down the build rate, increasing labor and equipment maintenance costs. This
20 problem interferes with the potential speed advantage of increased printing capability presented by the plurality of spray nozzles.

In addition to the above-mentioned disadvantages, the powders, especially metallic powders, used in both selective laser sintering and liquid binder techniques present safety issues that render them undesirable for use in an office environment. These safety issues may
25 require special clothing and processing facilities to prevent, for example, skin contact or inhalation of toxic materials. In addition, more expense may be incurred through complying with regulations for the disposal of toxic materials. For these reasons, these techniques do not lend themselves to being used in typical office environments, such as architectural and design firms, or doctors' offices.

30 U.S. Pat. No. 5,490,962 to Cima discloses solid free-form techniques for making medical devices for controlled release of bioactive agents.

In another embodiment, the method involves applying, to a first portion of a first layer of particles, an aqueous fluid in an amount sufficient to react the particles with the aqueous fluid to the extent that the particles within the first portion crystallize to form an essentially solid, singular article. A second layer of the particles is formed on the first layer. An aqueous fluid is applied to a first portion of the second layer of the particles in an amount sufficient to react the particles with the aqueous fluid, to the extent that the particles within the first portion of the second layer crystallize to form an essentially solid, singular article from the first portion of the first layer and the first portion of the second layer.

These and other features, aspects and advantages of the present invention will become better understood with reference to the following description and appended claims.

BRIEF DESCRIPTION

In the drawings:

FIG. 1 is a graph of the relationship between plaster strength and water content of a plaster;

FIG. 2 illustrates schematically a first layer of a mixture of particulate material of the invention deposited onto a downwardly movable surface on which an article is to be built, before any fluid has been delivered;

FIG. 3 illustrates schematically an ink-jet nozzle delivering an activating fluid to a portion of the layer of particulate material of FIG. 2 in a predetermined pattern;

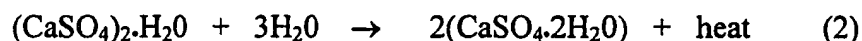
FIG. 4 illustrates schematically a view of a final article made from a series of steps illustrated in FIG. 3 enclosed in the container while it is still immersed in the loose unactivated particles; and

FIG. 5 illustrates schematically a view of the final article from FIG. 4.

DETAILED DESCRIPTION

The present invention relates to a 3DPTTM material system comprising a mixture of an aqueous fluid and a particulate material that includes plaster. The aqueous fluid contains water that hydrates the plaster contained in the particulate material, to form an essentially solid article. Various processing aids may be added to either the particulate material, the aqueous fluid, or both, including, but not limited to, accelerators, adhesives, flowrate enhancers, humectants, and visible dyes. The present invention also relates to a method of using such a materials system, and to an article made by the method of the invention. The

insoluble particles. The interlocking of crystals is responsible for a great deal of the eventual physical strength of the set plaster. Conventionally, during the period in which the plaster sets up, any physical disturbance to the setting plaster should be minimized, or the plaster may not achieve its potential maximum strength, because the minute crystals of gypsum will not completely interlock. When mixed with sufficient water, plaster recovers the 1½ parts of water it possessed prior to calcination of the gypsum, and sets to a solid material of substantially the same composition as gypsum. When properly calcined, plaster is fairly insoluble in cold water and only slightly soluble in warm water. For example, at room temperature, about one part of plaster is soluble in about 400 parts of water. The rehydration, or re-crystallization of plaster, after it has been mixed with water, is referred to as "setting," and proceeds according to the following equation (2):



As shown in FIG. 1, the strength of a plaster-based article increases substantially after about 93% of the free moisture has been removed. Therefore, subsequent to crystallization, or setting, all of the water in excess of that required for crystallization is removed by accelerated drying or by the natural slow evaporation of the moisture to increase the strength of the final article. The time for removal of the excess water will vary with the type of plaster, the ratio of water to plaster, atmospheric moisture, temperature, and air circulation.

As described above, the material system of the present invention includes a mixture of an aqueous fluid, and a particulate material that includes plaster. For purposes of the present invention, "particulate material" is meant to define any material containing significant amounts of plaster, and which may additionally include other materials, such as, but not limited to, accelerators, adhesives, flowrate enhancers, humectants, visible dyes, fiber, and filler. Examples of these and other additives may be found in U.S. Application Serial No. 08/707,693, filed September 4, 1996, which is hereby incorporated by reference in its entirety. Generally, the size of the particles in the particulate material is limited by the thickness of the layers to be printed. That is, the particles are preferably approximately smaller than the thickness of the layers to be printed. Using smaller particles may provides advantages such as smaller feature size, the ability to use thinner layers, and the ability to reduce what is known in the art as a "stair stepping" effect. In preferred embodiments, the material system includes particulate material having particles with a mean diameter ranging from about 10 µm to about 300 µm, more preferably ranging from about 10 µm to about 100 µm, and more preferably ranging from about 10 µm to about 50 µm.

amount of distortion in the final article. Preferably, the individual droplets of aqueous fluid have a volume ranging from about 30 pl to about 200 pl. Two commercially available print heads provide droplet sizes ranging from about 70 pl to about 90 pl, and from about 110 pl to about 130 pl. Typically, the material system and method of the present invention are capable
5 of producing features on the order of about 75-125 μm , but smaller or larger features may be achieved by changing the droplet size.

Once the aqueous fluid is printed onto the particulate material layer, a process which is described in more detail below, the water contained in the aqueous fluid immediately begins to evaporate and to diffuse away from the location where it was printed. Maximizing
10 the amount of aqueous fluid printed to the layers ensures that sufficient water for the rehydration of the plaster may be drawn from the fluid before it evaporates or migrates, and also because the fluid acts as a vehicle in which the reaction may take place. The aqueous fluid is capable of bonding together the particulate material in an amount that is several times the mass of a droplet of the fluid. The amount by which the individual droplets expand or
15 migrate into the particulate material depends on many factors, including the rate at which the water and the plaster react, and may also be affected by the addition of additives to either the particulate material and/or the aqueous fluid.

In other embodiments, either the particulate material, the aqueous fluid, or both, may include one or more processing aids. For example, in the present invention, it is essential that
20 the plaster set as quickly as possible. Therefore, to facilitate quick setting, accelerators are frequently used. "Accelerator," as used herein, is meant to define any material that increases the rate at which plaster sets. Examples of ways to accelerate the rate of plaster include, but are not limited to, increasing the solubility of plaster in water, or by providing additional nucleation sites for crystal formation. Accelerators are generally used sparingly in
25 conventional plaster processing, as they may adversely affect the strength characteristics of the plaster. However, accelerators are preferred in the present invention due to the importance of having the plaster set quickly. Suitable accelerators include, but are not limited to, Terra Alba, potassium sulfate, sodium chloride, under calcined plaster, alum or potassium alum, lime, and calcined lime. Terra Alba, which is raw ground gypsum, is a
30 preferred accelerator, and works by providing additional nucleation sites for gypsum crystal formation. Another preferred accelerator is potassium sulfate, which is thought to work by increasing the solubility of the plaster in the water. Both Terra Alba and potassium sulfate also increase the final strength of the article. In one embodiment, at least one accelerator is

article. Those of ordinary skill in the art may select suitable adhesives through routine experimentation. Particulate adhesives may be screened or comminuted to the desired size, which is typically less than about 170 mesh, and preferably less than about 175 mesh.

Preferably, the adhesive, or combination of adhesives, is at least partially water soluble, and more preferably substantially water soluble. It appears that there is a synergistic relationship in the techniques of the invention between the plaster and a water soluble adhesive, by which the setting plaster draws water from the adhesive solution, causing the adhesive to set more rapidly. As the aqueous fluid dissolves, partially dissolves, activates, or reacts with the adhesive, the viscosity of the aqueous fluid increases dramatically, arresting further migration of the aqueous fluid from the initial point of impact. Within a few minutes, the aqueous fluid with adhesive dissolved therein infiltrates the only slightly soluble plaster particles and/or crystallized gypsum crystals, forming adhesive bonds therebetween.

As stated previously, an adhesive, or adhesives, may be added to the particulate material and/or the aqueous fluid. In the present embodiment, the adhesive is preferably a water soluble resin, such as, but not limited to, polyvinyl alcohol, (PVA), polyvinyl pyrrolidone (PVP), or dextrin. In addition to adding strength to the final article, the addition of a water soluble adhesive resin may also reduce distortion in comparison to parts bound together solely by water, or by a water soluble adhesive. When any of the previously described adhesives are added to the particulate material, the amount of adhesive in the particulate material is dependent on the type of adhesive and plaster used, and may be determined by routine experimentation. In the embodiment where an adhesive or combination of adhesives is added to the particulate material, it is preferably added in an amount of less than about 50 %, and more preferably in an amount of about 20 % to about 40 %, by weight of the particulate material. When an adhesive or combination of adhesives is added to the aqueous fluid, it is preferably added in a ratio of about 10%, by weight of the fluid.

Referring now to FIGS. 2 and 3, a schematic representation of a printing method using the materials system of the present invention is presented. According to the method, a layer of particulate material 20 is applied on a downwardly movable surface 22 of a container 24. The layer of particulate material 20 may be formed in any manner, and preferably is applied using a counter-roller, which minimizes disruption of any previously applied layers. The thickness of an individual layer used to build the prototype articles of the present invention preferably range from about 12 μm to about 125 μm , more preferably from about

The previous steps of applying a layer of particulate material, applying the aqueous fluid, and indexing the movable surface downward are repeated until the final article is completed. Alternatively, those skilled in this art would know how to build an article in layers upward from an immovable platform, by successively depositing, smoothing and printing a series of such layers. FIG. 4 is a schematic representation of a final cylindrical article after it has been completely formed. At the end of the process, only the top surface 34 of a final article 38 is visible in the container. The final article is preferably completely immersed in a bed 36 of undissolved and unreacted particulate material, and is made up of a plurality of essentially evenly distributed layers.

FIG. 5 is a schematic representation of the final cylindrical article 38 after removal of undissolved and unreacted particulate material, preferably by blown air or a vacuum. After removal of the undissolved and unreacted particulate material from the final article 38, post-processing treatment may be performed, including cleaning, infiltration with stabilizing materials, painting, etc.

After the final article has been formed, any additional water, or free moisture, must be removed to increase the strength of the printed article. As stated previously, the strength of plaster will increase only slightly until about 93% of the free moisture has been removed, after which the strength increases sharply. Although not required, excess moisture may be removed from the final article by drying at a temperature of at least about 125 °F, generally up to a limit of around 350°F. If an adhesive is incorporated into the article, higher drying temperatures may be used, which is dependent on the adhesive used. In general, when an adhesive is used, the flexural strength of the final article increases with the amount of time it is subject to heat.

After the final article has set, and all loose surrounding powder has been removed, the article may be infiltrated with a variety of materials to improve the hardness, strength, or toughness. These finishes may fill in any pores in the part, improving the surface finish, and making it more impervious to water or solvents. Suitable hardeners include, but are not limited to, molten wax, varnish, lacquer, cyanoacrylate, polyurethane, and epoxy.

A final article formed using the material system and methods of the present invention will include a plurality of evenly distributed layers of the reaction product of the particulate material and the aqueous fluid. The reaction product of the particulate material and the aqueous fluid preferably includes a substantial amount of hydrated plaster, which may vary depending on the particulate material used. In preferred embodiments, the reaction product

various additives may be included in the particulate material and/or aqueous fluid to accelerate the rate at which the plaster sets.

The plaster may also be evaluated to determine the ease of spreading. Simple test parts may also be formed to determine, inter alia, the flexural strength, the distortion, the rate of setting, the optimum layer thickness, and the optimum ratio of water to plaster (or aqueous fluid to particulate material).

Material systems suitable for use in the 3DP™ method include those having reaction products with minimal distortion, in addition to relatively high flexural strength. That is, reaction products with high flexural strength values may not be suitable for use in the 3DP™ method, because distortions may compromise the accuracy of the final printed articles, which is especially applicable where relatively fine features are desired.

EXAMPLES

A type of test part that may be formed and used to evaluate the flexural strength of a material system for screening purposes is referred to as a "break bar." Break bars used herein were formed by spreading successive layers of particulate material to which successive applications of an aqueous fluid were made, until the fluid permeated several of the layers. The break bars were then allowed to set. These bars were sawed into 0.2" strips. The flexural strength of the material was determined, in megapascals (MPa), by breaking the bar with a testing device. The qualitative assessment of a material system also involves visually inspecting the parts for distortion.

EXAMPLES 1-3

Several materials were screened as described above, and used to form break bars. The results of the break bar tests are shown below in Table 1. Four different types of plaster or particulate material were used. The aqueous fluid used in the first example included about 95 % water and about 5 % of a humectant, glycerol. An accelerator was added to the aqueous fluid used in the example, which included about 92 % water, about 5% glycerol, and about 3% of the accelerator, potassium sulfate. In most instances, the addition of an aqueous fluid improved the flexural strength of the materials, as illustrated by a comparison of the flexural strength measurements from the first and second examples.

EXAMPLE 4

One kilogram of particulate material was prepared using the materials and ratios shown below in Table 2. The adhesives were sieved through a 170 mesh screen into a bucket, prior to mixing together by hand with the plaster and accelerator. After hand mixing
5 with the plaster and accelerator, the mixture was placed in a Waring Model 34BL22 Commercial Blender with a two (2) gallon mixing vessel and blended on "high" for about 30 seconds. The resulting blended mixture was then sieved through a 50 mesh screen to remove clumps.

TABLE 2

Ingredient	Percent	Material/Trade Name	Vendor
Plaster	79.2	White Hydrocal Cement	U.S. Gypsum
Accelerator	20.0	Dextrin	Staley/Star-dri5
Accelerator	0.8	Terra Alba	U.S. Gypsum

10

About 2 liters of the aqueous fluid were prepared using the amounts shown in Table 3 below.

TABLE 3

Ingredient	Percent	Material/Trade Name	Vendor/Grade
Water	86.2	Distilled	Poland Spring
Humectant	6.0	Glycerol	Aldrich
Flow Rate Enhancer	5.0	PVP	Aldrich
Accelerator	2.0	Potassium Sulfate	Aldrich
Enhances Solubility of PVP	0.5	Isopropyl Alcohol	Osco Drug
Flow Rate Enhancer	0.3	Ethyl Butyrate	Aldrich

15 A break bar and two (2) depowdering bars, were formed from the particulate mixture and an aqueous fluid. The break bar strength was about 18.5 MPa. The break bar had a warping distortion of 0.001", and the edges were curled. The depowdering bars were printed with layers having a thickness of about 3 mil, at a ratio of about 47% aqueous fluid to powder, by volume. Loose powder was removed from 10/19 and 11/19 holes in each of the
20 two depowdering bars.

The results shows the synergistic effect on the break bar strength of the addition of an accelerator and an adhesive to both the particulate material and the aqueous fluid. However, the material system was not optimal due to the distortion after printing.

EXAMPLE 6

One kilogram of particulate material was prepared using the amounts shown in Table 6 below. The adhesives were sieved through a 170 mesh screen into a bucket, prior to mixing together by hand with the plaster and accelerator. After hand mixing with the plaster and
5 accelerator, the mixture was placed in a Waring Model 34BL22 Commercial Blender with a two (2) gallon mixing vessel and blended on "high" for about 30 seconds. The resulting blended mixture was then sieved through a 50 mesh screen to remove clumps, hair, dirt, etc.

TABLE 6

Ingredient	Percent	Material/Trade Name	Vendor/Grade
Plaster	79.2	White Hydrocal Cement	U.S. Gypsum
Adhesive	17.5	Dextrin	Staley/Star-dri 5
Adhesive	2.5	Cellulose Gel	FMC Avicel RCN-30
Accelerator	0.8	Terra Alba	U.S. Gypsum

10 About 2 liters of the aqueous fluid was prepared using the amounts shown in Table 7 below. An accelerator, two (2) flowrate enhancers, a humectant, and a substance to increase the solubility of the flow rate enhancers were added to a clean jug, followed by distilled water, and the jug was capped and shaken until the ingredients were dissolved.

TABLE 7

Ingredient	Percent	Material/Trade Name	Vendor/Grade
Water	86.2	Distilled	Poland Spring
Humectant	6.0	Glycerol	Aldrich
Flow Rate Enhancer	5.0	PVP	Aldrich
Accelerator	2.0	Potassium Sulfate	Aldrich
Enhances Solubility of PVP	0.5	Isopropyl Alcohol	Osco Drug
Flow Rate Enhancer	0.3	Ethyl Butyrate	Aldrich

15 A break bar and two (2) depowdering bars were formed from the particulate mixture and the aqueous fluid, as described above. The break bar strength was about 8.5 MPa, with a distortion of about 2 mils. The depowdering bars were printed with layers having a thickness of about 3 mil, and a ratio of about 49 % aqueous fluid to particulate material. Loose powder
20 was removed from 8/19 and 7/19 holes in each of the two depowdering bars.

article, and some of which was loose. When the build was finished, the excess powder was vacuumed away and the prototype article was lifted from the bed for viewing. The article was sanded and infiltrated with ZR10 cyanoacrylate resin and cured for about 30 minutes to produce a harder finish than that of the test parts of Experiment 5.

- 5 Those skilled in the art will readily appreciate that all parameters listed herein are meant to be exemplary and actual parameters depend upon the specific application for which the methods and materials of the present invention are used. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the appended claims and equivalents thereto, the invention can be practiced
- 10 otherwise than as specifically described.

What is claimed is:

12. The product of claim 4, wherein said adhesive is at least partially water-soluble.
13. The product of claim 8, wherein said adhesive is at least partially water-soluble.
14. The product of claim 11, wherein said adhesive is at least partially water-soluble.
15. The product of claim 1, wherein the thickness of each of said layers is less than about
5 300 μm .
16. The product of claim 1, comprising a flexural strength of at least 1 MPa.
17. A product of the reaction of the mixture of:
a particulate material including plaster and an accelerator; and
an aqueous fluid;
10 said plaster reacted with at least a portion of said aqueous fluid to form an essentially
solid article including hydrated plaster;
said article including a plurality of essentially evenly distributed layers of said reaction
product.
18. A product of the reaction of the mixture of:
15 a particulate material including plaster and an adhesive; and
an aqueous fluid;
said plaster reacted with at least a portion of said aqueous fluid to form an essentially
solid article including hydrated plaster, said adhesive adhered to at least portions of said
hydrated plaster.
- 20 19. A method for forming an article, comprising:
providing a first layer of a particulate material including plaster;
dispensing an aqueous fluid onto said first layer;
allowing at least a portion of said plaster and at least a portion of said aqueous fluid to
react to form an at least partially solid first layer;
25 providing a second layer of said particulate material on said at least partially solid first
layer;
dispensing said aqueous fluid onto said second layer; and

AMENDED CLAIMS

[received by the International Bureau on 21 March 2000 (21.03.00);
original claims 1, 4, 8, and 11 amended; remaining claims unchanged (1 page)]

1. A product of the reaction of the mixture of:
a particulate material including plaster;
an aqueous fluid; and
an adhesive;
said plaster reacted with at least a portion of said aqueous fluid to form an essentially solid article including hydrated plaster;
said article including a plurality of essentially evenly distributed layers of said reaction product.
2. The product of claim 1, wherein said aqueous fluid includes an accelerator.
3. The product of claim 2, wherein said aqueous fluid includes less than about 5 percent of said accelerator, by weight of said aqueous fluid.
4. The product of claim 1, wherein said aqueous fluid includes said adhesive, and said adhesive is adhered to at least portions of said hydrated plaster.
5. The product of claim 4, wherein said aqueous fluid includes less than about 10 % of said adhesive, by weight of said aqueous fluid.
6. The product of claim 1, wherein said particulate material includes an accelerator.
7. The product of claim 6, wherein said particulate material includes less than about 5 % of said accelerator, by weight of said particulate material.
8. The product of claim 1, wherein said particulate material includes said adhesive, said adhesive adhering to at least portions of said hydrated plaster.
9. The product of claim 8, wherein said particulate material includes less than about 50 % of said adhesive, by weight of said particulate material.
10. The product of claim 1, wherein said particulate material and said aqueous fluid each include an accelerator.
11. The product of claim 10, wherein said particulate material and said aqueous fluid each

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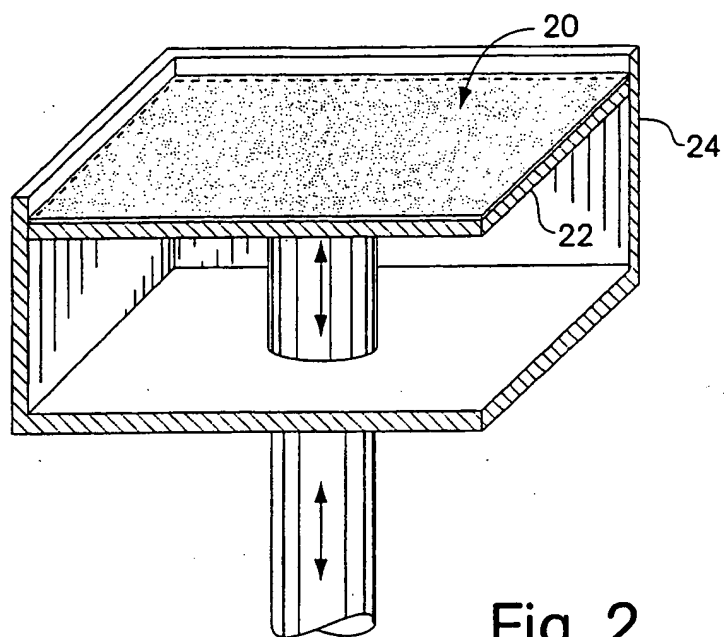


Fig. 2

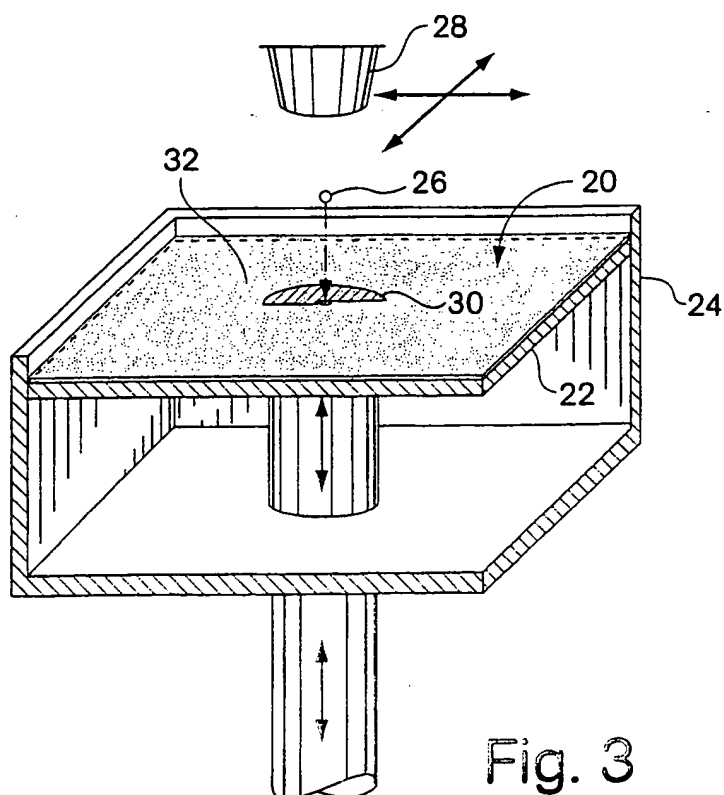


Fig. 3

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/20628

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B32B31/00 B28B7/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B29C B28B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication where appropriate, of the relevant passages	Relevant to claim No
X	WO 97 11835 A (3D SYSTEMS INC) 3 April 1997 (1997-04-03)	1, 17, 19, 24, 26
Y	page 50, line 7,8; claims 1-110 ---	18
X	US 4 247 508 A (HOUSHOLDER ROSS F) 27 January 1981 (1981-01-27) column 4, line 26-46; figure 10 ---	1
Y	DE 40 12 044 A (HEIDELBERGER ZEMENT AG) 17 October 1991 (1991-10-17) claim 2 ---	18
A	WO 97 26302 A (MASSACHUSETTS INST TECHNOLOGY) 24 July 1997 (1997-07-24) the whole document --- -/--	1-28

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

Special categories of cited documents

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

14 January 2000

Date of mailing of the international search report

21/01/2000

Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/20628

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9711835	A	03-04-1997	AU 7376696 A	17-04-1997
			AU 7550396 A	17-04-1997
			BR 9610663 A	13-07-1999
			BR 9610750 A	13-07-1999
			CA 2233202 A	03-04-1997
			CA 2233225 A	03-04-1997
			CN 1202131 A	16-12-1998
			EP 0852535 A	15-07-1998
			EP 0852536 A	15-07-1998
			JP 11512662 T	02-11-1999
			WO 9711837 A	03-04-1997
			US 5943235 A	24-08-1999
US 4247508	A	27-01-1981	NONE	
DE 4012044	A	17-10-1991	NONE	
WO 9726302	A	24-07-1997	US 5660621 A	26-08-1997
			US 5851465 A	22-12-1998
US 5204055	A	20-04-1993	CA 2031562 A,C	09-06-1991
			DE 69025147 D	14-03-1996
			DE 69025147 T	05-09-1996
			EP 0431924 A	12-06-1991
			JP 2729110 B	18-03-1998
			JP 6218712 A	09-08-1994
			US 5340656 A	23-08-1994
			US 5807437 A	15-09-1998
			US 5387380 A	07-02-1995
US 5340656	A	23-08-1994	US 5204055 A	20-04-1993
			CA 2031562 A,C	09-06-1991
			DE 69025147 D	14-03-1996
			DE 69025147 T	05-09-1996
			EP 0431924 A	12-06-1991
			JP 2729110 B	18-03-1998
			JP 6218712 A	09-08-1994
			US 5807437 A	15-09-1998
			US 5387380 A	07-02-1995
WO 9325336	A	23-12-1993	US 5387380 A	07-02-1995
			CA 2136748 A	23-12-1993
			EP 0644809 A	29-03-1995
			JP 2862674 B	03-03-1999
			JP 7507508 T	24-08-1995

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